**657.** *The Preparation, Properties, Structure, and Spectra of 12-Tungstochromic*(III) *Acid.*

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Existence of a 12-heteropolytungstate with chromium(III) as the central ion has been confirmed and its properties examined. The chromium appears to exist in an undistorted tetrahedral environment, a structure confirmed by the visible spectrum. The lower stability of this compound than of 12-tungstoferrates(III) and 12-tungstocobaltates(III) is interpreted in terms of crystal-field stabilisation energies.

SATURATING a sodium paratungstate solution with a solution of chromium nitrate in water results in a deep green solution and a green precipitate. By this procedure, Knorre [1] and Kantschew [1,2] prepared heteropolytungstates, but of different compositions. Rosenheim [3] suggested that these were not true heteropolytungstates. Mair and Waugh [4] prepared an acid which they identified through its salts as probably an 11-acid. Previous work [5,6] has shown that analytical techniques alone are sometimes not adequate to identify a heteropolytungstate and that an $X$-ray structural determination and analysis of the spectrum are necessary. By these methods, the product obtained from the saturation of sodium paratungstate solution with chromium nitrate solution has now been examined.

EXPERIMENTAL

A solution of sodium tungstate (56·2 g. in 300 ml. of water) was converted into the para-form by addition of N-nitric acid (194·4 ml.) and treated, while boiling, with chromium nitrate (9 g.) in water (500 ml.) with stirring, during 4—6 hr. A green precipitate was formed. Cooling and filtration gave a green solution, which was treated with ether (stirring) and then slowly with 12N-sulphuric acid (400 ml.). The lowest of the three layers formed was the light green ether addition compound of 12-tungstochromic acid mixed with a little of the ether addition compound of metatungstic acid. The mixture had density *ca.* 2·2 and the average yield in terms of sodium tungstate was ∼20%. On dilution with water, the ether separated and was removed in a current of air. The aqueous solution was then repeatedly evaporated to dryness and extracted with water until all the metatungstic acid was decomposed. This process also decomposed some of the tungstochromic acid, but enough survived from each run to prepare at least 1 g. of a salt. The salts were prepared by precipitation with solutions of the corresponding chlorides.

Thermogravimetric analysis was carried out on a Stanton thermogravimetric balance running at a chart-speed of 6 in./hr. The energies of activation for the loss of water and the decomposition of the anion were calculated by the method described by Freeman and Carrol [7] for a system involving a solid decomposing into a solid and a gas. This involved plotting $[\Delta(1/T)/\Delta \log x]$ against $[\Delta \log (- \mathrm{d}x/\mathrm{d}t)]/(\Delta \log x)$ where $T$ was the absolute temperature and $x$ the number of molecules of water at temperature $T$. This plot gave a straight line with slope $-E/2\cdot3R$ where $E$ was the energy of activation.

An $X$-ray powder photograph of the cæsium salt was taken by mounting the specimen in a fine Lindemann glass tube and using Cu-$K_\alpha$ radiation. The intensities were measured by inspection. The spectra were taken on a Optika recording spectrophotometer.

Barium was determined as sulphate by precipitation with dilute sulphuric acid; chromium by oxidation to chromate, reduction with an excess of ferrous sulphate, and back-titration; tungsten by precipitation with cinchonine hydrochloride and ignition to the oxide; ammonia

[1] Knorre, *Chem. Ztg.*, 1910, **34**, 406.
[2] Kantschew, *Chem. Ztg.*, 1912, **36**, 199.
[3] Rosenheim, Abegg's " Handbuch," Vol. IV, Part 1, 1050.
[4] Mair and Waugh, *J.*, 1950, 2372.
[5] Brown and Mair, *J.*, 1958, 2597.
[6] Brown and Mair, *J.*, 1962, 1512.
[7] Freeman and Carrol, *J. Phys. Chem.*, 1958, **62**, 394.

by distillation into standard acid; water by ignition and difference; potassium by difference; and guanidine by the micro-Dumas method.

*Results.*—Tungstochromic(III) acid is very soluble in water. Its green solution is slowly decomposed by water and rapidly by strong alkali. Thermal analysis of the free acid showed two regions where loss of weight occurred. For the first, around 120°, the energy of activation was 7 kcal. mole$^{-1}$ and for the second, around 250°, 35 kcal. mole$^{-1}$. The latter value represented both loss of water and decomposition of the heteropoly-anion since, after heating to 200°, some of the anion could still be extracted with water whereas, after heating to 250°, only free $Cr^{3+}$ ions were identified. In both cases, water was lost in accordance with a first-order reaction.

The following salts, prepared as described above, were purified by recrystallisation from water: *potassium salt* (Found: $K_2O$, 6·3; $Cr_2O_3$, 2·25; $WO_3$, 80·0; $H_2O$, 11·4. $2·5K_2O,\frac{1}{2}Cr_2O_3,12WO_3,20H_2O$ requires $K_2O$, 6·8; $Cr_2O_3$, 2·2; $WO_3$, 80·6; $H_2O$, 10·4%); *ammonium salt* [Found: $(NH_4)_2O$, 4·1; $Cr_2O_3$, 2·4; $WO_3$, 85·8; $H_2O$, 6·85. $2·5(NH_4)_2O,\frac{1}{2}Cr_2O_3,12WO_3,12H_2O$ requires $(NH_4)_2O$, 4·1; $Cr_2O_3$, 2·4; $WO_3$, 86·8; $H_2O$, 6·7]; *guanidine salt* [Found: $(CH_6N_3)_2O$, 10·8; $Cr_2O_3$, 2·23; $WO_3$, 82·8; $H_2O$, 6·0. $2·5(H_6CN_3)_2O,\frac{1}{2}Cr_2O_3,12WO_3,10H_2O$ requires $(CH_6N_3)_2O$, 10·1; $Cr_2O_3$, 2·25; $WO_3$, 82·35; $H_2O$, 5·3%]; *barium salt* (Found: BaO, 10·8; $Cr_2O_3$, 2·2; $WO_3$, 80·0; $H_2O$, 6·2. $2·5BaO,\frac{1}{2}Cr_2O_3,12WO_3,12H_2O$ requires BaO, 11·1; $Cr_2O_3$, 2·2; $WO_3$, 80·5; $H_2O$, 6·2%).

The results of the X-ray powder photography are shown in the Table, with the results obtained for cæsium 12-tungstoferrate. These figures show that the photographs were almost identical and that the structures must therefore be similar.

Lines and intensities for cæsium 12-tungstochromate(III) and 12-tungstoferrate(III).

| $h^2 + k^2 + l^2$ | Chromate | | Ferrate | $h^2 + k^2 + l^2$ | Chromate | | Ferrate |
| | Calc. | Obs. | Obs. | | Calc. | Obs. | Obs. |
|---|---|---|---|---|---|---|---|
| 6 | 13·7 | 15 | 15 | 32 | 86·7 | 90 | 90 |
| 8 | 5·8 | 5 | 5 | 33 | 10·2 | 10 | 10 |
| 10 | 25·7 | 25 | 25 | 34 | 9·1 | 10 | 10 |
| 12 | 150·0 | 150 | 150 | 36 | 15·1 | 15 | 15 |
| 14 | 0·9 | Absent | Absent | 38 | 92·1 | 90 | 90 |
| 16 | 79·9 | 70 | 75 | 40 | 2·1 | Absent | Absent |
| 18 | 17·6 | 20 | 17 | 41 | 28·9 | 30 | 25 |
| 20 | 0·2 | Absent | Absent | 42 | 47·5 | 50 | 45 |
| 22 | 94·5 | 90 | 90 | 44 | 78·9 | 80 | 80 |
| 24 | 11·8 | 10 | 10 | 46 | 2·7 | Absent | Absent |
| 26 | 79·9 | 90 | 80 | 48 | 29·5 | 30 | 30 |
| 27 | 8·8 | 10 | 10 | 50 | 20·3 | 200 | 210 |
| 30 | 46·7 | 50 | 50 | | | | |

The ultraviolet, visible, and near-infrared spectra of tungstochromic acid in aqueous solution showed peaks at 38,400 ($\varepsilon$ 9·9 × 10$^4$), 16,000 ($\varepsilon$ 105), and 8300 cm.$^{-1}$ ($\varepsilon$ 20). The second peak was broad; the other two were fairly sharp. The peak at 38,400 cm.$^{-1}$ was obtained in the spectra of every 12-heteropolytungstic acid so far examined and was probably due to the polytungstate ion itself. The peak at 8300 cm.$^{-1}$ was probably due to the $^4T_1(F) \longrightarrow {}^4T_2(F)$ transition and the peak at 16,000 cm.$^{-1}$ to the $^4T_1(F) \longrightarrow {}^4A_2$ transition. For a $\Delta$ value of 8300 cm.$^{-1}$, a third peak should appear around 19,000 cm.$^{-1}$, corresponding to the $^4T_1(F) \longrightarrow T_1(P)$ transition, but this was not observed, owing to a failure to resolve the broad band at 16,000 cm.$^{-1}$ or more probably to a masking effect of the very much more intense polytungstate peak at 38,400 cm.$^{-1}$. These results agree with the postulated tetrahedral structure of the central chromium(III) ion. The value of $\Delta$ (8300 cm.$^{-1}$) is close to that expected for a tetrahedral $Cr^{3+}$ ion, *viz.*, $\frac{4}{9}$ of 17,400 cm.$^{-1}$ = 7730 cm.$^{-1}$. The corresponding heteropolymolybdate formed is a 6-molybdochromate; [8] the main peak of its spectrum occurs at 17,500 cm.$^{-1}$, *i.e.*, close to that recorded for chromium hexahydrate for the $^4A_{2g} \longrightarrow {}^4T_{2g}(F)$ transition. This agrees with the postulated six co-ordinated chromium ion.

## DISCUSSION

The analytical results suggest that the heteropolytungstic acid formed is a 12-acid. This is confirmed by the X-ray and spectra data. 12-Tungstochromic acid is, however,

[8] Rosenheim and Schwer, *Z. anorg. Chem.*, 1914, **89**, 224.

much more difficult to prepare than 12-tungstoferric(III),[6] 12-tungstozincic(II),[5] 12-tungsto-cobaltic(III), and 12-tungstocobaltic(II) acid.[9]   This can best be understood by considering the mechanism of formation.   Tungstate ions by themselves tend to polymerise on acidification to the 12-acid, *i.e.*, metatungstic acid.   Certain ions can be involved in this polymerisation and occupy a site in the middle of the polymerised tungstate ion.   This site is limited by four oxygen ions of the tungstate lattice situated tetrahedrally about it.   Thus, the central ion, if it is a transition metal, moves from the distorted octahedral hydrate to the tetrahedral environment of the heteropoly-acid.   According to McLure[10] the preference energy for octahedral rather than tetrahedral sites for chromium(III) is 46·7 kcal. mole$^{-1}$.   This value, deduced from the crystal-field stabilisation energies, is much larger than those of iron(III) (0 kcal. mole$^{-1}$), cobalt(III) (19 kcal. mole$^{-1}$), cobalt(II) (2·1 kcal. mole$^{-1}$), and zinc(II) (0 kcal. mole$^{-1}$).   Thus the tendency for chromium(III) to enter a tetrahedral environment from an octahedral one is less than for those other ions and would account for the relative difficulty of preparation and the low yields.   Similarly the decomposition equilibrium between the 12-tungstochromic anion and probably chromic and tungstic oxide will proceed at a lower temperature.   This also was found experimentally. The decomposition temperature of the acid, around 250°, was lower than those of 12-tungstocobaltic(III) (370°) and 12-tungstoferric acid (390°).

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[9] Baker and McCutcheon, *J. Amer. Chem. Soc.*, 1956, **78**, 4503.
[10] McLure, *J. Phys. and Chem. Solids*, 1957, **3**, 311.